

Electron Transfer Integral between Two Zero-Overlap States

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ABSTRACT

In the research of electron transfer (ET) reactions, the theoretical calculation of the ET matrix element V_{BA} is of special importance. Some examples in which the two electron-localized states have a zero overlap were found. Thus, a new procedure for V_{BA} calculation was developed and applied to the investigation of the donor-acceptor 90° oriented ET reactions. This procedure, which is a supplement necessary to the recently developed approach suitable for a nonorthogonal case, was derived in detail. To check the rationality of the zero value of V_{BA} in the reaction $O_2O_2^- \rightarrow O_2^-O_2$, the angle dependence of S_{BA} and V_{BA} between two electron-localized states was calculated. © 1996 by John Wiley & Sons, Inc.

Introduction

As a kind of "simplest chemical reactions," electron transfer (ET) processes have been widely investigated both in theory and in experiments. A key quantity in all the different ET models is the ubiquitous many-electron transfer matrix element, V_{BA} , defined as¹

$$V_{BA} = (1 - S_{BA}^2)^{-1} [H_{BA} - S_{BA}(H_{BB} + H_{AA})/2] \quad (1)$$

within the two-state model. In eq. (1), $S_{ij} = \langle \Phi_i | \Phi_j \rangle$, $H_{ij} = \langle \Phi_i | H | \Phi_j \rangle$ ($i, j = A, B$); Φ_A and Φ_B are the two electron-localized quasidiabatic UHF wave functions representing the reactant state and the product state, respectively; and H is the total electronic Hamiltonian. An approach to the theoretical calculation of V_{BA} when Φ_A and Φ_B are nonorthogonal,² was developed and published,³ and a set of program modules were linked to

HONDO by Farazdel and Dupuis.⁴ Unfortunately in some special geometries of the donor-acceptor system, there exist a zero overlap between Φ_A and Φ_B , and an abnormal computation will be performed by using this method. We call such an orthogonality a "pseudo-orthogonality" because it depends on the geometry of the system without a need for a standard orthogonalization. Two examples, in which the donor-acceptor is in 90° orientation,⁵ are shown in Figure 1. To carry out the normal computation of V_{BA} in the case of pseudo-orthogonality, a new procedure is necessary.

Computational Strategy

STATEMENT OF PROBLEM

For the diagonalization of the overlap matrix,^{2,3} the unitary transformations

$$\hat{a} = aV, \quad \hat{b} = bU \quad (2)$$

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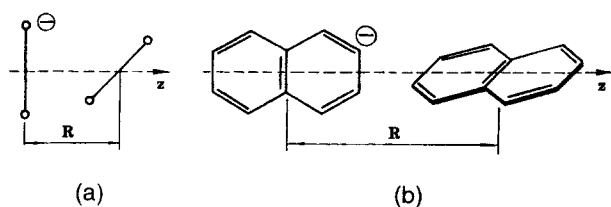


FIGURE 1. Two ET systems which have a zero overlap due to the pseudo-orthogonality of Φ_A and Φ_B . The donor-acceptor pair is at 90° orientation. O is oxygen and NA is naphthalene. (a) $O_2^- - O_2$ (C_{2v}); (b) $NA^- - NA$ (C_{2v}).

were performed on the sets of symmetry-broken electron-localized quasidiabatic UHF wave functions a ($a = a_1, a_2, \dots, a_N$), and b ($b = b_1, b_2, \dots, b_N$) (see appendix of ref. 3 and section II of ref. 2). N is the number of electrons in the donor-acceptor system, and a diagonalized overlap matrix between two new sets \hat{a} and \hat{b} can be written as

$$\hat{d} = \int \hat{b}^+ \hat{a} d\tau = U^+ \left(\int b^+ a d\tau \right) V. \quad (3)$$

Expanding a and b in terms of a common set χ ($\chi = \chi_1, \chi_2, \dots, \chi_M$), i.e.,

$$a = \chi A, \quad b = \chi B, \quad (4)$$

and defining a so-called generalized density matrix P (see ref. 2 for detail) and a factor

$$\text{prod} = \prod_{i=1}^N \hat{d}_{ii}, \quad (5)$$

Farazdel et al. gave the one-electron contribution $\Omega_{BA}^{(1)}$ and the two-electron contribution $\Omega_{BA}^{(2)}$ so that^{3,4}

$$H_{BA} = \Omega_{BA}^{(1)} + \Omega_{BA}^{(2)} \quad (6)$$

with

$$\Omega_{BA}^{(1)} = (\det U)(\det V^+) \sum_{\mu\nu} P_{\mu\nu} \omega_{\mu\nu}, \quad (7)$$

and

$$\begin{aligned} \Omega_{BA}^{(2)} = & (1/2)(\det U)(\det V^+)(\text{prod})^{-1} \\ & \times \sum_{\mu}^M \sum_{\nu}^M \sum_{\lambda}^M \sum_{\sigma}^M P_{\mu\nu} P_{\lambda\sigma} \\ & (\langle \mu\nu | \lambda\sigma \rangle - \langle \mu\sigma | \lambda\nu \rangle). \end{aligned} \quad (8)$$

In eqs. (7) and (8), $\omega_{\mu\nu}$ and $\langle \mu\nu | \lambda\sigma \rangle$ are the one-electron integrals and the two-electron integrals, respectively.

When a zero overlap exists between Φ_A and Φ_B , the above treatment fails in calculation because of the zero value of the prod factor in eq. (8), and V_{BA} becomes infinite.

SOLUTION METHOD

It was noticed that the zero overlap occurs when one of the \hat{d}_{ii} in eq. (8) is zero. Supposing that \hat{d}_{zz} has a zero value, i.e.,

$$\hat{d}_{zz} = \langle \hat{b}_z | \hat{a}_z \rangle = 0, \quad (9)$$

and noticing that \hat{a}_z and \hat{b}_z are not eigenfunctions of H , we can write eq. (22) in ref. 2 or eq. (A-7) in ref. 3 as

$$\begin{aligned} \Omega_{BA}^{(1)} = & (\det U)(\det V^+) \\ & \times \left[\sum_{i \neq z}^N \langle \hat{b}_i | w(1) | \hat{a}_i \rangle \left(\prod_{k \neq i, z}^N \hat{d}_{kk} \right) \hat{d}_{zz} \right. \\ & \left. + \langle \hat{b}_z | w(1) | \hat{a}_z \rangle \left(\prod_{k \neq z}^N \hat{d}_{kk} \right) \right] \\ = & (\det U)(\det V^+) \left(\prod_{k \neq z}^N \hat{d}_{kk} \right) \sum_{\mu\nu}^M \hat{B}_{z\mu}^+ \hat{A}_{\nu z} \omega_{\mu\nu} \end{aligned} \quad (10)$$

where $w(1)$ denotes the one-electron operator, and \hat{A} and \hat{B} are the transformations, i.e.,

$$\hat{a} = \chi \hat{A}, \quad \hat{b} = \chi \hat{B}.$$

On the other hand, the two-electron contribution [eq. (23) of ref. 2] can be expressed as

$$\begin{aligned} \Omega_{BA}^{(2)} = & (\det U)(\det V^+) \\ & \times \sum_{i < j}^N \left(\sum_{k \neq i, j}^N \hat{d}_{kk} \right) \langle \hat{b}_i \hat{b}_j | w(1, 2) (1 - P_{12}) | \hat{a}_i \hat{a}_j \rangle \\ = & (1/2)(\det U)(\det V^+) \left[\sum_{i \neq z}^N \sum_{j \neq z}^N \left(\sum_{k \neq i, j, z}^N \hat{d}_{kk} \right) \right. \\ & \times \hat{d}_{zz} \langle \hat{b}_i \hat{b}_j | w(1, 2) (1 - P_{12}) | \hat{a}_i \hat{a}_j \rangle \\ & + 2 \sum_i^N \left(\prod_{k \neq i, z}^N \hat{d}_{kk} \right) \\ & \left. \times \langle \hat{b}_i \hat{b}_z | w(1, 2) (1 - P_{12}) | \hat{a}_i \hat{a}_z \rangle \right] \end{aligned}$$

$$\begin{aligned}
&= (\det U)(\det V^+) \sum_{\mu}^M \sum_{\nu}^M \sum_{\lambda}^M \sum_{\sigma}^M \sum_i^N \left(\prod_{k \neq i, z}^N \hat{d}_{kk} \right) \\
&\quad \hat{B}_{i\mu}^+ \hat{B}_{z\nu}^+ \hat{A}_{\lambda i} \hat{A}_{\sigma z} \langle \mu\nu | w(1,2)(1 - P_{12}) | \lambda\sigma \rangle
\end{aligned} \quad (11)$$

where P_{12} is the usual permutation operator, and $w(1,2)$ denotes the Coulombic interaction between electrons 1 and 2. If we use the alternative notation

$$\begin{aligned}
\langle \mu\lambda | \nu\sigma \rangle &= \langle \mu\nu | w(1,2) | \lambda\sigma \rangle \\
&= \langle \chi_{\mu}(1) \chi_{\nu}(2) (1/r_{12}) \chi_{\lambda}(1) \chi_{\sigma}(2) \rangle
\end{aligned}$$

eq. (11) may be written as

$$\begin{aligned}
\Omega_{BA}^{(2)} &= (\det U)(\det V^+) \\
&\quad \times \sum_{\mu}^M \sum_{\nu}^M \sum_{\lambda}^M \sum_{\sigma}^M \left[\langle \mu\lambda | \nu\sigma \rangle \sum_i^N \left(\prod_{k \neq i, z}^N \hat{d}_{kk} \right) \right. \\
&\quad \left. \hat{B}_{i\mu}^+ \hat{B}_{z\nu}^+ (\hat{A}_{\lambda i} \hat{A}_{\sigma z} - \hat{A}_{\sigma i} \hat{A}_{\lambda z}) \right].
\end{aligned} \quad (12)$$

In eqs. (10) and (12) the sum is over both the α set and the β set of UHF self-consistent field (SCF) molecular orbitals. In the case of pseudo-orthogonality, $S_{BA} = S_{BA}^{\alpha} \times S_{BA}^{\beta} = 0$ and $V_{BA} = H_{BA}$.^{1a} Combining eqs. (1), (6), (10), and (12), we have

$$\begin{aligned}
V_{BA} &= (\det U)(\det V^+) \left\{ \left(\prod_{k \neq z}^N \hat{d}_{kk} \right) \sum_{\mu\nu}^M B_{z\mu}^+ A_{\nu z} \omega_{\mu\nu} \right. \\
&\quad + \sum_{\mu}^M \sum_{\nu}^M \sum_{\lambda}^M \sum_{\sigma}^M \left[\langle \mu\lambda | \nu\sigma \rangle \sum_i^N \left(\prod_{k \neq i, z}^N \hat{d}_{kk} \right) \right. \\
&\quad \left. \left. \hat{B}_{i\mu}^+ \hat{B}_{z\nu}^+ (\hat{A}_{\lambda i} \hat{A}_{\sigma z} - \hat{A}_{\sigma i} \hat{A}_{\lambda z}) \right] \right\}.
\end{aligned} \quad (13)$$

Examples and Results

Based on our treatment described previously, a modification in the ET package of HONDO-8 was made. In the computation of the ET transfer matrix element V_{BA} for the systems given in Fig. 1, the geometry of $O_2^- - O_2$ encounter complex is optimized at the level of 6-31G + sp diffuse function (the exponent is 0.0845)⁶ under the C_{2v} symmetry constraint. Detailed discussions for this ET reaction were made previously.⁵ On the other hand naphthalene (NA) and the anion (NA^-) as shown in Fig. 1b are separately optimized at the level of 3-21G under the constraint of D_{2h} (Fig. 2), and computed equilibrium bond lengths and bond angles of the donor (NA^-) and the acceptor (NA) are

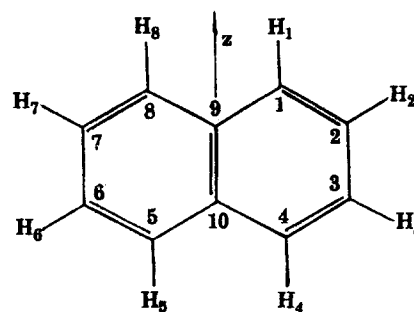


FIGURE 2. D_{2h} symmetry (the principal axis coincide with the z axis) in the optimization of naphthalene.

listed in Table I. The geometry where two diabatic potential energy surfaces cross is determined by using a linear reaction coordinate

$$Q_i = (Q_i^B + Q_i^A)/2. \quad (14)$$

In eq. 14, Q_i is the i th nuclear coordinate, and B and A refer to the product and the reactant, respectively. It is easy to see that the geometry determined by eq. (14) forms two degenerate electron-localized states ($H_{BB} = H_{AA}$). An electron-localized initial guess was used to induce the UHF SCF calculation. For these two systems, the zero value of S_{BA} is unchangeable no matter what basis set is used and what value of R is taken (R is the distance between the centers of the donor and the acceptor, see Fig. 1). Values of V_{BA} were calculated without considering the symmetry (Table II).

To check the rationality of our procedure and results, we let the angle of the orientation for the donor and the acceptor of $O_2^- - O_2$ vary from 0° to 90° at a step length of 10° for the ET reaction $O_2 - O_2^- \rightarrow O_2^- - O_2$ (Fig. 1a). The angle dependences of S_{BA} and V_{BA} are shown in Figure 3. It can be seen from the curves in Figure 3 that the zero values of S_{BA} and V_{BA} in the donor-acceptor 90° orientation case turn out to be reasonable ones.

TABLE I.
Computed Equilibrium Bond Lengths (nm) and Bond Angles ($^\circ$) of Naphthalene (NA) and Anion (NA^-).

| Bond Lengths | NA | NA^- | Bond Angles | NA | NA^- |
|--------------|--------|--------|-----------------------|-------|--------|
| C_1C_2 | 0.1357 | 0.1404 | $\angle C_1C_9C_{10}$ | 119.0 | 117.9 |
| C_1C_9 | 0.1410 | 0.1411 | $\angle C_2C_1C_9$ | 120.8 | 121.4 |
| C_9C_{10} | 0.1409 | 0.1453 | $\angle H_1C_1C_9$ | 118.8 | 118.7 |
| C_2C_3 | 0.1414 | 0.1372 | $\angle H_2C_2C_1$ | 120.3 | 119.5 |
| C_1H_1 | 0.1073 | 0.1074 | $\angle C_1C_2C_3$ | 120.3 | 120.4 |
| C_2H_2 | 0.1072 | 0.1076 | | | |

TABLE II.
ET Integrals for Two Examples.

| $D-A$ | R^a | E_t^b | P_D^c | P_A | S_{BA}^a | S_{BA}^b | $V_{BA} \text{ (HND)}^d$ | $V_{BA} \text{ (MHD)}^e$ |
|---------------|--------|------------|---------|-------|------------|------------|--------------------------|--------------------------|
| $O_2^- - O_2$ | 0.3354 | -299.09653 | -1.0 | 0.0 | 0.96 | 0.0 | ∞ | 0.0 |
| $NA^- - NA$ | 0.8000 | -762.36083 | -1.0 | 0.0 | 0.0 | 0.96 | ∞ | 0.0 |

^a Distance between the centers of donor and acceptor (nm).

^b Total energy (au).

^c Net charge condensed to the donor (P_D) and the acceptor (P_A).

^d Calculated by using the HONDO-8 program.

^e Calculated by using HONDO program modified by the authors.

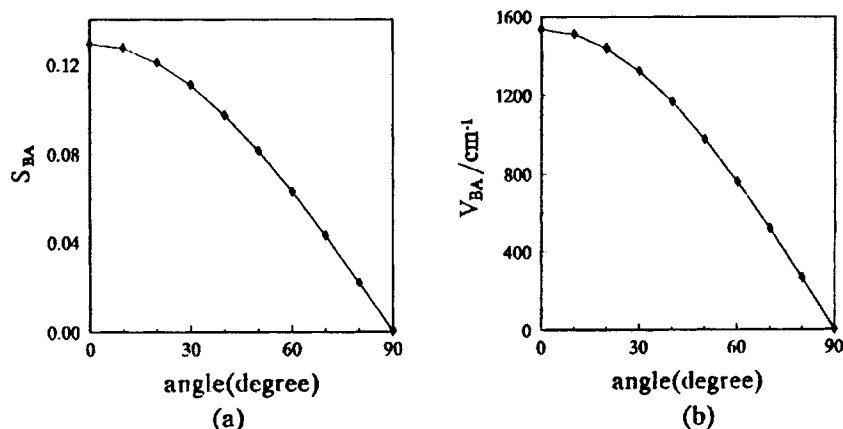


FIGURE 3. Influences of orientation upon (a) S_{BA} and (b) V_{BA} for the electron transfer between O_2^- and O_2 . Step length is 10° .

An alternative approach to the zero values of V_{BA} is to show that Φ_A and Φ_B belong to different irreducible representations according to the applied symmetry (if any); but in general the ET integrals are calculated without considering the symmetry because an inappropriately applied symmetry may cause other problems in the ET integral calculation. When a zero overlap appears, direct computations of V_{BA} from eq. (13) are always valid no matter whether symmetry is applied or not.

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